

Simultaneous Removal of Surfactant Template from MCM-41 and Implantation of Transition Metal Complexes into Mesopores with Supercritical Fluid

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Abstract: The simultaneous removal of up to 92% of the surfactant template and chemical implantation of transition metal complexes into mesopores has been successfully achieved by treating as-synthesized pure siliceous MCM-41 with supercritical CO₂ modified with CH₂Cl₂/MeOH mixture, resulting in the formation of functionalized material with uniform pore structure.

Keywords: MCM-41, mesoporous, supercritical fluids, transition metal complexes.

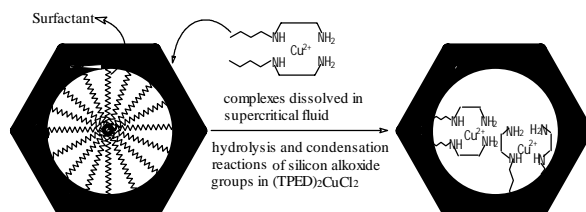
Since the discovery of the M41S family by Mobil scientists in 1992^{1,2}, synthesis and application of ordered mesoporous materials using surfactants as pore-directing agents has attracted wide attention³. Among this family of materials, MCM-41 is studied more extensively. It possesses regularly hexagonal arrays of cylindrical mesopores and changeable pore diameter between 1.5-20 nm. These properties make MCM-41 materials to be the best candidates of catalyst or catalyst support⁴, and the hosts for many guest materials⁵. The preparation of MCM-41 materials usually includes a high temperature calcination for destroying the surfactant template. This procedure may open mesopores as well as easily cause structure shrinkage⁶. It has been reported that the template molecules in MCM-41 could be removed by extraction with the ethanol solution of an acid or salt⁷. The main drawback lies in its low extraction efficiency or/and negative effect on the pore structure. Supercritical fluids, particularly CO₂, as a substitute solvent has been used widely in aerogel chemistry, organic synthesis and extraction of natural products⁸, due to their liquid-like solvation properties and gas-like physical properties. However, few attempts at the modification of porous materials has been reported by using supercritical fluids as reaction media⁹.

The present work describes a new method for rapidly removing the surfactant template from as-synthesized MCM-41 material and simultaneous implantation of transition metal complexes into mesopores using supercritical CO₂ modified with

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$\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture as solvent (**Scheme1**). The resulted new materials show uniform pore structure.

Scheme 1



The parent MCM-41 was prepared in the similar method by using cetyltrimethylammonium bromide (CTAB) as the template¹⁰. The white solid product obtained was washed with deionized water at ambient temperature and dried for 24 h at 373 K in vacuum. Three unmodified samples were used: MCM-41U (uncalcined as-synthesized mesoporous material), MCM-41C (the same sample but calcined at 823 K), and MCM-41E (the same sample but extracted with the supercritical fluid at 368 K and 30 MPa for 6 h). The as-synthesized material with template molecules inside the mesopores was functionalized in a one-step process that includes simultaneous removal of the template and implantation of di-N-[3-(trimethoxysilyl)propyl]ethylenediamine Copper(II) dichloride $\{(\text{TPED})_2\text{CuCl}_2$ as model transition metal complex $\}$ into mesopores with the same supercritical fluid at 368 K and 30 MPa for 12 h. The functionalized material was Soxhlet-extracted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture for 24 h to remove the trace of free copper(II) complexes sticking to the surface and dried in vacuum at 373 K for 10 h. The Cu^{2+} uptake was analyzed by atomic absorption method after HF digestion of the functionalized materials. The functionalized sample with Cu^{2+} uptake of 3.73% was designated as MCM-41EF. For a comparison, MCM-41EF was further calcined at 823 K, and the resulted material was designated as MCM-41FC.

Figure 1 Powder X-ray diffraction patterns of the series of MCM-41 materials.

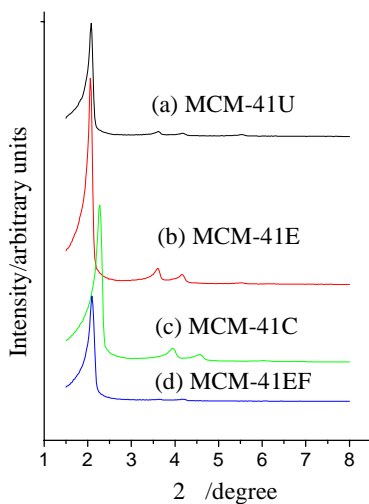
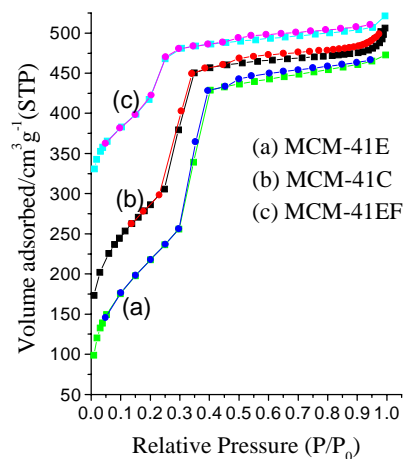


Figure 2 Nitrogen adsorption (squaresymbol) and desorption (circle symbols) at 77 K.



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Small-angle X-ray powder diffraction (SAXRD) patterns for the series of MCM-41 samples are shown in **Figure 1**. All of the samples display three or four reflection peaks that are assigned to the (100), (110), (200) and (210) reflection of hexagonally ordered MCM-type structures with unit cell parameters between 4.5 and 4.9 nm. The d_{100} values and the positions of all reflection peaks for uncalcined samples are similar to the as-synthesized sample MCM-41U, indicating that pore contraction did not occur during the removal of the template and simultaneous modification of mesopores by supercritical fluid treatment. On the other hand, the copper(II) complexes inside MCM-41 make with contribution to the decrease of peak intensity for the low-angle reflections. Compared to the uncalcined samples, all peaks shift slightly to higher angles and their d-values all decrease for the calcined samples. This is probably due to the contraction of the frameworks, which may arise from the high temperature calcination.

The adsorption-desorption isotherms (**Figure 2**) of N_2 at 77 K are of type IV for the series of MCM-41 samples which is typical of mesoporous materials. The parameters calculated from nitrogen adsorption data using BJH method are listed in the **Table 1**, and the pore size distributions of these samples are present in **Figure 3**. The lower BET surface area, pore diameter and pore volume for MCM-41EF indicate that Copper(II) complex should be confined in the mesopores of MCM-41. Furthermore, the success in chemical implantation of the complex into mesopores was confirmed by the data of FTIR (**Figure 4**). The functionalization with $(TPED)_2CuCl_2$ resulted significant decrease in the peak intensity at about 3700 cm^{-1} ascribed to silanol (SiOH) groups, indicating the replacement of surface SiOH groups by the functional molecules *via* covalent linkage. The inflection point in the isotherm of MCM-41EF becomes less sharp and shifts to lower pressure. This shift indicates the presence of smaller mesopores due to the impregnation of the copper complex.

Table 1 Properties of the series of MCM-41 molecular sieves

Sample	Removal efficiency ^a of template molecules (%)	d_{100} (nm)	Lattice parameter (nm)	Pore diameter (nm)	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})
MCM-41U	—	4.25	4.91	—	—	—
MCM-41E	97	4.25	4.91	3.05	892	0.902
MCM-41C	—	3.94	4.55	2.76	866	0.829
MCM-41EF	92	4.24	4.90	2.18	691	0.528
MCM-41FC	—	3.97	4.58	2.59	789	0.694

^aEfficiency was determined by means of TGA method for comparing the mass loss between the as-synthesized sample and after the supercritical fluid treatment.

Finally, we have also succeeded in anchoring other transition metal (Co^{2+} , Ni^{2+} , Zn^{2+} , Pd^{2+} *etc.*) complexes inside MCM-41 by this method.

Summarizing, the present study demonstrates that the supercritical fluids are ideal media for rapidly removing the template molecules from the mesopores and simultaneous functionalizing the mesoporous material. The proposed method could be proved interest from several points of view. First of all, the template in as-synthesized

MCM-41 material can be rapidly and almost quantitatively removed from mesopores. Secondly, it provides a very effective approach to functionalize mesoporous as well as microporous materials without pore blocking because of the enhanced diffusivity of the functional molecules in supercritical fluids and accelerated reaction kinetics. Finally, such a procedure greatly simplifies functionalization of MCM-41 material and pore opening, can avoid structure shrinkage during the high temperature calcination. The method described may be also applied to molecular imprinting of mesoporous materials for obtaining novel selective adsorption^{11,12}.

Figure 3 The pore size distribution of the series MCM-41 materials

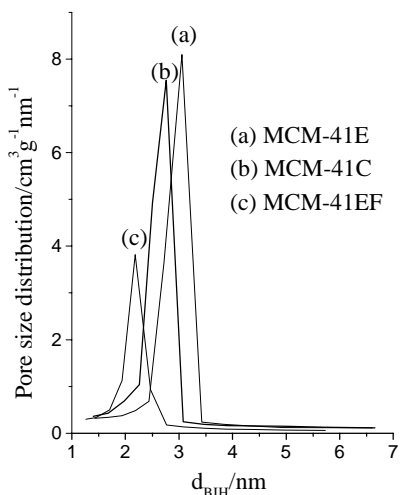
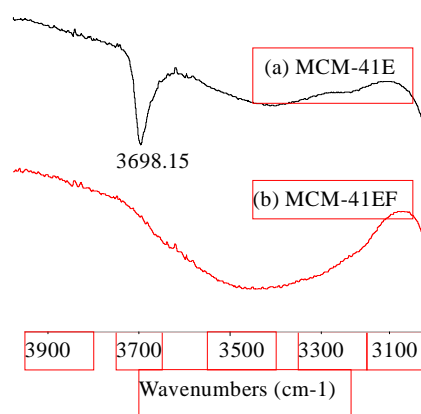


Figure 4 FTIR spectra of the series of MCM-41 materials.



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